(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 March 2002 (28.03.2002)

PCT

(10) International Publication Number
WO 02/24829 A1

(51) International Patent Classification[7]: C09K 5/04

(21) International Application Number: PCT/GB00/03596

(22) International Filing Date:
19 September 2000 (19.09.2000)

(25) Filing Language: English

(26) Publication Language: English

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

**Published:**
— *with international search report*

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

WO 02/24829 A1

(54) Title: CENTRIFUGAL COMPRESSION REFRIGERANT COMPOSITIONS

(57) Abstract: A liquid refrigerant composition is disclosed which comprises at least 35 % by weight of tetrafluoroethane and at least 20 % by weight of heptafluoropropane such that the sum of the concentrations of heptafluoroethane and heptafluoropropane is at least 90 % by weight of the composition.

# CENTRIFUGAL COMPRESSION REFRIGERANT COMPOSITIONS

This invention relates to refrigerant compositions. More particularly, it relates to refrigerant compositions which can be used in place of R12 in a compression refrigeration system employing a centrifugal compressor.

R12 ($CCl_2F_2$) has been used for many years as a refrigerant composition. However, in view of concerns over the use of CFC gases various attempts have been made to reduce or eliminate its use. In other words, ways have been sought to replace R12 by formulations which are not damaging to the environment.

One hydrocarbon which has been used with some success instead of R12 is tetrafluoroethane (R134). This is because it has a similar pressure-temperature relationship and refrigerating effect to that of R12. Indeed in positive displacement compressors R134 is a good substitute for R12.

Unfortunately, it is not satisfactory to use R134 instead of R12 in systems involving the use of a centrifugal compressor. This is because an additional constraint is placed on the refrigerant in that, as well as having similar thermodynamic properties, it must also have similar vapour density properties. Roughly, vapour densities are related to the molecular weight. The molecular weight of R12 is 121 whereas the molecular weight of R134 is only 102. This difference would require the dimensions of the impellor used in the centrifugal compressor system to be altered as well as its speed. Clearly there is a need for a composition which can be used in an existing system without modification.

A further complication in the use of refrigerants using a centrifugal compressor resides in the fact that a centrifugal compressor uses a "flooded" evaporator i.e. some refrigerant liquid remains throughout the cooling cycle. As a result, the formulation of the liquid composition included in the system generally differs from the formulation of the vapour circulating in the system.

The object of the present invention is to provide a refrigerant composition

which can be used in systems employing a centrifugal compressor without the need to modify the impellor dimensions or its speed. Clearly there is a need for a composition which can be used in an existing system without modification.

According to the present invention it has surprisingly been found that certain liquid formulations of R134 and R227 (heptafluoropropane) behave well as replacements for R12 in centrifugal compression refrigerating systems. According to the present invention there is provided a liquid refrigerant composition which comprises at least 35% by weight of tetrafluoroethane and at least 20% by weight of heptafluoropropane such that the concentration of tetrafluoroethane and heptafluoropropane is at least 90% by weight of the composition.

Tetrafluoroethane exists in two forms, namely the symmetrical 1,1,2,2-tetrafluoroethane and 1,1,1,2-tetrafluoroethane known as R134a. The latter is preferred for use in the present invention.

Likewise heptafluoropropane exists in two isomeric forms, namely 1,1,1,2,3,3,3-heptafluoropropane, known as R227ea which is preferred, and 1,1,1,2,2,3,3-heptafluoropropane, known as R227ca.

As indicated above the formulation in the vapour phase will differ from that in the liquid phase. It has been found that formulations comprising 20 to 52% by weight of R227 and, correspondingly, 80 to 48% of R134a will provide formulations which will behave in the vapour phase in a manner similar to that of R12 with a variation of + or - 10%.

The preferred compositions of the present invention consist essentially of R134 and R227 (i.e. they are binary compositions), especially R134a and R227ea, but small amounts of a third component can be included. Any additional component i.e. third or higher component can be present in an amount up to 10% weight, preferably up to 5%, and more preferably up to 2%, by weight of the composition. If more than one additional component is used then the total amount of these components is not more than 10% by weight. Since a principal aim of the formulation is to increase the overall molecular weight and thereby increase the vapour density, it is more usual to replace some of the R134a than replace some

of the R227. Possible additional components include C318 (octafluorocyclobutane), R218 (octafluoropropane) and R125 (pentafluoroethane). The concentration of R134 is generally 80 to 35%, preferably 70 to 45% and more preferably 50 to 60%, by weight. The concentration of R227 is generally 20 to 65%, preferably 30 to 55% and especially 40 to 50%, by weight. A particularly preferred formulation consists of 52.5% of R134a and 47.5% of R227ea. This preferred formulation is based on the assumption that one needs to obtain a formulation which has an overall molecular weight corresponding to that of R12 i.e. 121. This is achieved with a vapour formulation of about 60% R134a and 40% R227ea.

However, as indicated above, molecular weight alone does not give a complete picture of how a formulation will behave in the vapour phase. It is also necessary for it to have the correct vapour density and vapour pressure characteristics.

Other preferred formulations have been found which attempt to take this into account; these contain less than or equal to 45% by weight of R227, especially 30 to 40, 42.5 or 45%, preferably 35 to 42.5 or 45% or 35 to 40%, by weight, the remainder being R134. A particularly preferred formulation comprises about 63.3% by weight of R134a and about 36.7% by weight of R227ea. These formulations are cheaper to make because R227ea is more expensive than R134a.

The present invention also provides a method of refrigerating a body which comprises placing the object in the vicinity of a refrigeration system which employs a centrifugal compressor wherein the liquid refrigerant supplied to the compressor is a composition of the present invention, and a refrigeration system incorporating a centrifugal compressor wherein the liquid in the compressor is a composition of the present invention.

The following Examples further illustrate the present invention:-

| | Composition / % w/w | | Comments |
|---|---|---|---|
| Blend | R134a | R227ea | |
| Example 1 | 52.5 | 47.5 | Liquid phase composition |
| Example 2 | 60.0 | 40.0 | Co-existing vapour phase of Example 1. |
| Example 3 | 63.3 | 36.7 | Liquid phase composition |
| Example 4 | 68.0 | 32.0 | Co-existing vapour phase of Example 3 |

Saturated Liquid Vapour Pressure Comparison

| Temperature | Pressure / bar | | | | |
|---|---|---|---|---|---|
| °C | R12 | Example 1 | Example 2 | Example 3 | Example 4 |
| -20 | 1.510 | 1.306 | 1.359 | 1.282 | 1.292 |
| -10 | 2.193 | 1.922 | 1.997 | 1.940 | 1.954 |
| 0 | 3.089 | 2.749 | 2.853 | 2.832 | 2.852 |
| 10 | 4.236 | 3.833 | 3.974 | 4.010 | 4.038 |
| 20 | 5.674 | 5.226 | 5.413 | 5.528 | 5.566 |
| 30 | 7.446 | 6.980 | 7.224 | 7.442 | 7.493 |
| 40 | 9.594 | 9.152 | 9.465 | 9.813 | 9.882 |

Comparison of Vapour Density.

| Temperature | Vapour Density / kg/m$^3$ | | |
|---|---|---|---|
| °C | R12 | Example 2 | Example 4 |
| -10 | 12.92 | 11.35 | 11.14 |
| 0 | 17.87 | 16.35 | 16.04 |
| 10 | 24.18 | 22.98 | 22.52 |
| 20 | 32.13 | 31.62 | 30.97 |
| 30 | 42.07 | 42.81 | 41.90 |
| 40 | 54.42 | 57.23 | 55.99 |

Refrigeration Performance

| Temperature | R12 | | Example 2 | |
|---|---|---|---|---|
| °C | Capacity/kW | COP | Capacity/kW | COP |
| -25 | 0.535 | 1.702 | 0.520 | 1.837 |
| -20 | 0.734 | 1.983 | 0.704 | 2.101 |
| -15 | 0.981 | 2.322 | 0.934 | 2.428 |
| -10 | 1.274 | 2.718 | 1.210 | 2.817 |
| -5 | 1.615 | 3.170 | 1.533 | 3.269 |
| 0 | 2.003 | 3.680 | 1.903 | 3.784 |
| 5 | 2.437 | 4.247 | 2.318 | 4.361 |

As can be seen, the formulations of Examples 2 and 4 give particularly good vapour pressure and vapour density values which are comparable to, or even better than, those of R12, especially at 30°C to 40°C which are generally the most important as these are the usual condensing temperatures.

## CLAIMS

1. A liquid refrigerant composition which comprises at least 35% by weight of tetrafluoroethane and at least 20% by weight of heptafluoropropane such that the sum of the concentrations of heptafluoroethane and heptafluoropropane is at least 90% by weight of the composition.

2. A composition according to claim 1 which consists essentially of tetrafluoroethane and heptafluoropropane.

3. A composition according to claim 1 or 2 wherein the tetrafluoroethane is 1,1,1,2-tetrafluoroethane.

4. A composition according to claim 1 wherein the heptafluoropropane is 1,1,1,2,3,3,3-heptafluoropropane.

5. A composition according to claim 1 which consists essentially of 80 to 35% by weight of tetrafluoroethane and 20 to 65% by weight of heptafluoropropane.

6. A composition according to claim 5 which consists essentially of 70 to 45% by weight of tetrafluoroethane and 30 to 55% by weight of heptafluoropropane.

7. A composition according to claim 6 which consists essentially of 60 to 50% by weight of tetrafluoroethane and 40 to 50% by weight of heptafluoropropane.

8. A composition according to claim 1 which consists essentially of about 52.5% by weight of tetrafluoroethane and about 47.5% by weight of heptafluoropropane.

9. A composition according to claim 6 which comprises less than 45% by weight of heptafluoropropane.

10. A composition according to claim 9 which consists essentially of 35 to 45% by weight of heptafluoropropane.

11. A composition according to claim 9 which consists essentially of 35 to 40% by weight of heptafluoropropane.

12. A refrigeration system incorporating a centrifugal compressor wherein

the liquid in the compressor is a composition as claimed in claim 1.

13. A method of refrigerating a body which comprises placing the object in the vicinity of a refrigeration system which employs a centrifugal compressor wherein the liquid refrigerant supplied to the compressor is a composition as claimed in claim 1.

# INTERNATIONAL SEARCH REPORT

Int'l onal Application No
PCT/GB 00/03596

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K5/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 13 June 2001 | 25/06/2001 |

| Name and mailing address of the ISA | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,<br>Fax: (+31-70) 340-3016 | Puetz, C |

Form PCT/ISA/210 (second sheet) (July 1992)

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